Proceedings of the
American Control Conference
San Francisco, California • June 1993

Multiple Steady States in Homogeneous Azeotropic Distillation

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Abstract

In this article we study multiple steady states in ternary homogeneous azeotropic distillation. We show that in the case of infinite reflux and an infinite number of trays, multiple steady states exist when the distillate flow varies non-monotonically along the continuation path of the bifurcation diagram with the distillate flow as the bifurcation parameter. We derive a necessary and sufficient condition for the existence of these multiple steady states based on the geometry of the distillation region boundaries. We also locate in the composition triangle the feed compositions that lead to these multiple steady states. We show that the prediction of the existence of multiple steady states in the case of infinite reflux and an infinite number of trays has relevant implications for columns operating at finite reflux and with a finite number of trays. Using numerically constructed bifurcation diagrams for specific examples, we show that these multiplicities tend to vanish for small columns and/or for low reflux flows.

1 Introduction

Azeotropic distillation is one of the most widely used and most important separation operations in the chemical and the specialty chemical industry. Among their surprising features, it has been discovered that such columns can exhibit multiple steady states i.e. two or more steady states with different composition and temperature profiles which correspond to the same set of operating parameters. In this article we are only investigating this type of *multiplicities*.

The term "homogeneous azeotropic distillation" covers the general notion of distillation of azeotrope forming mixtures where a single liquid phase exists in the region of interest. Unless stated otherwise, we use the following convention to refer to a given mixture: L (I, H respectively) corresponds to the component which has the lowest (intermediate, highest resp.) boiling point; we also denote the entrainer by E. The locations of the feed, distillate and bottoms in the composition triangle are denoted by F, D and B respectively. The corresponding flowrates are denoted by the same letters in italics (F, D, B, E and R for the reflux flow). Finally, we assume that the reader is familiar with the notions of residue curves, residue curve maps and distillation region boundaries (Doherty and Perkins, 1978).

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2 Infinite Reflux and Infinite Number of Trays

In this section we present an extensive analysis of the case where the reflux and the number of trays are infinite (the ∞/∞ case hereafter). The idea for examining this situation came from the multiplicities reported by Laroche et al. (1992) for the homogeneous mixture of acetone (L), heptane (H) and benzene (I). Laroche et al. (1992) report two different stable steady state profiles with identical feed compositions and flows, number of trays and distillate, bottom, reflux and reboil flow rates. In this column, the reflux to feed and the reflux to distillate flow ratios are very high - in the order of 100. Moreover, the column has 64 theoretical trays which is quite a large number. This suggests that this multiplicity may occur at infinite reflux and in columns with a large number of trays (infinite number of trays in the limit).

At infinite reflux, column profiles coincide with residue curves. In the special case of columns with an infinite number of trays there is one additional requirement: The column profile should include a pinch point. There are three types of candidate pinch points in any residue curve map, namely saddles, stable nodes and unstable nodes. Therefore, in the ∞/∞ case, the only acceptable columns belong to one of the following types:

I. Columns whose distillate composition is that of an unstable node. In this case, the column profile starts from the unstable node (top of the column), follows a residue curve and ends at an arbitrary point on the same residue curve (bottom product).

II. Columns whose bottom product composition is that of a stable node. In this case, the column profile starts from an arbitrary point in the composition triangle (top product), follows the residue curve that passes through this starting point and ends at the stable node (bottom product).

III. Columns whose composition profiles run along the distillation boundaries and contain at least one saddle. In this case, the top and bottom products lie on the distillation boundaries.

In the ∞/∞ case, given a feed composition and a feed flowrate F, the only unspecified parameter is the distillate flow rate D. In order to find whether multiple steady states can occur (i.e. whether different column profiles correspond to the same value of D)

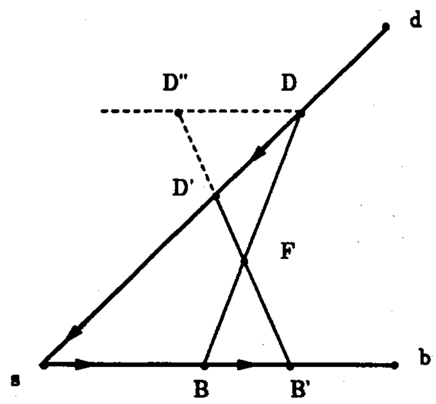

Figure 1: D increases monotonicaly for column profiles that contain only one saddle singular point.

we find all possible composition profiles by tracking the distillate and bottoms in the composition triangle, starting from the column profile with $D = 0$ (type I) and ending with the column profile with $D = F$ (type II). That is, we perform a bifurcation study (continuation of solutions) using the distillate flow as the bifurcation parameter. This task can be achieved because in the ∞/∞ case a continuation of solutions can be carried out based on physical arguments only.

It is easy to show that along the continuation path, first we track all possible type I column profiles, then those of type III and last all type II column profiles. It is apparent that if D increases monotonically along this "path" then a unique steady state exists for each value of D. Hence, the key feature that brings about the multiple steady states is that in a segment along this "path" *D decreases*. Therefore, in order to find rules for the existence of multiple steady states, we have to answer when D decreases along the continuation path. In this section, we assume that distillation boundaries are straight lines (this assumption will be dropped later). It can be easily proven that:

Fact 1 *Along the continuation path, D increases monotonically as we track all type I and type II column profiles.*

Therefore, a decrease in D can only occur as we track the type III column profiles i.e. columns whose composition profiles run along the edges of the distillation region where F is located and contain at least one of the saddle singular points. Next we will show the following:

Fact 2 *Along the continuation path, D increases monotonically for all type III column profiles that contain only one saddle singular point.*

Figure 1 shows a column profile (DsB) that contains only one saddle point (s). The lines ds and sb are distillation region boundaries. The arrows on ds and sb show the direction of the residue curves; this direction coincides with the direction of the continuation path. D'sB' is another, "later," column profile along this path. We examine what happens to D as we move from DsB to D'sB'. Draw the line that is parallel to BB' and passes through D. Name D'' the point where this line intersects the D'B' line. By construction, FB/DF = FB'/D''F. Since D''F>D' F then FB/DF < FB'/D' F. Therefore by the lever material balance rule, we conclude that D increases along the continuation path. This result is independent of the angle dsb, and therefore D increases monotonically for all type III column profiles that contain only one saddle singular point. Q.E.D.

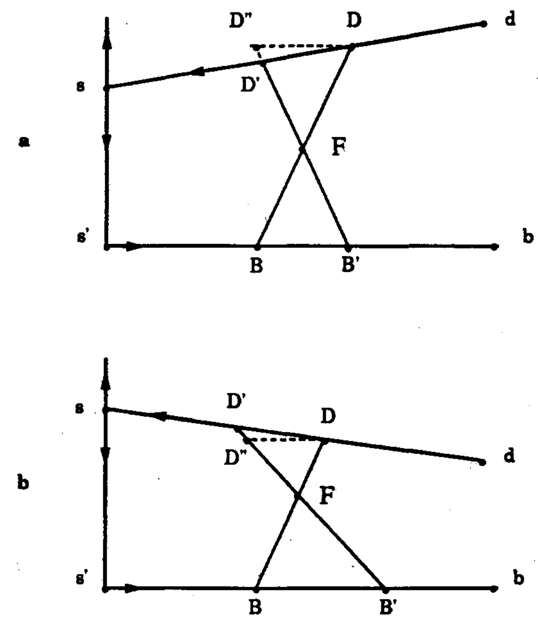

Figure 2: Geometry of the distillation region boundaries. a. D increases b. D decreases along the continuation path.

Note that fact 2 is equivalent to the following:

Fact 3 *A decrease in D can only occur as we track type III column profiles that contain at least two saddles.*

A consequence of fact 3 is that a necessary condition for the existence of this type of multiplicities is that the residue curve diagram contains at least two neighboring saddles. The situation of at least two neighboring saddles arises in 77 out of the 113 possible residue curve diagram classes. However, the aforementioned condition is not sufficient for the existence of multiple steady states.

Geometry of the Distillation Boundaries

The existence of multiplicities depends on the geometry of the distillation boundaries that form the two saddles. Figures 2a and 2b illustrate two cases of two neighboring saddles. The only difference between the two is the orientation of the ds distillation boundary. In order to check if D increases or decreases along the continuation path, the procedure used for the proof of fact 2 is applied. In Figure 2b, the line from D that is parallel to BB' crosses the D'B' line segment while it does not cross it in Figure 2a. Hence in Figure 2a, D''F > D'F while D''F < D'F in Figure 2b. As a result D increases in Figure 2a whereas D decreases in Figure 2b. Therefore multiple steady states exist only for the situation depicted in Figure 2b. Note

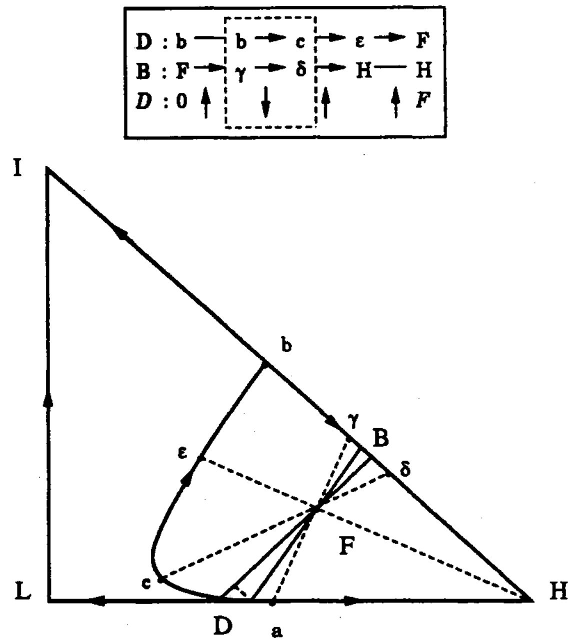

Figure 3: Highly curved boundaries can induce multiplicities.

that the existence of multiple steady states depends on the relative position of the boundaries ds and s′b while the location of the ss′ boundary does not play any role.

In summary, for the existence of multiplicities it is required that (*geometrical condition*): As we move along the continuation path from D to D′ and accordingly from B to B′, the line that passes from D and is parallel to BB′ crosses the D′B′ line segment.

Curved Boundaries

Hereafter, we consider the general case of curved boundaries. Distillation region boundaries that do not coincide with the sides of the composition triangle are often curved and in some cases highly curved. The following interesting result can be easily shown: if multiple steady states exist under the straight boundaries assumption, then, assuming that the azeotropic compositions do not change, these multiplicities still exist even if the boundaries are curved, although the appropriate feed region is changed. In the previous section we concluded that the occurence of two neighboring saddles is a necessary condition for multiplicities when boundaries are straight. This is not true in the general case of curved boundaries, because highly curved boundaries can function as "pseudo-saddles" and therefore can induce multiplicities.

Figure 3 shows a residue curve diagram with a highly curved boundary that separates the composition triangle in two distillation regions. If the boundary running from a to b were a straight line, there would not exist multiplicities for this mixture. The boundary ab is curved enough so that there exists a point c on it where the tangent to the boundary is parallel to the IH edge. Now, the geometrical condition can be applied to check for multiplicities. If D lies on ac then for any B on bH the geometrical condition is satisfied. Figure 3 shows the continuation path of all possible column profiles for a given feed. The ratio FB / DF and therefore D decreases as D moves from a to c and hence multiplicities exist. Similarly, the condition for multiplicities is satisfied if D lies on ac and the bottoms composition is any point on Ib. Note that the geometrical condition is not satisfied for any D′ but only for D′ sufficiently close to D.

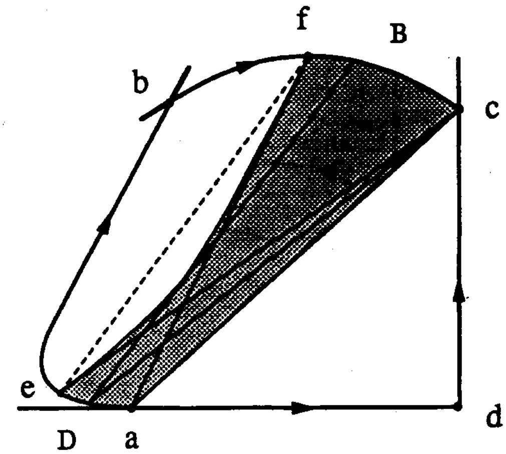

Figure 4: The appropriate feed region in the case of two curved boundaries.

Appropriate Feed Composition

The curvature of the boundary may affect the region of feed compositions that lead to multiplicities because the geometry of the boundaries is changed. The most general case where both D and B lie on curved boundaries is illustrated by Figure 4. In this figure, point e is the location on ab where the tangent to the ab boundary is parallel to the tangent to the bc boundary at point c. Similarly, f is the point on bc where the tangent to the bc boundary is parallel to the tangent to the ab boundary at point a. For some D on ab, there exist *some* B on bc that satisfy the geometrical condition. In general, for each D on ae there exists a *different set* S_B(D) of bottoms compositions that satisfies the geometrical condition. For example if D is located at point a then S_B(D) is the boundary segment fc while if D is located at e the S_B(D) is just the point c. Hence for each D the appropriate feed composition is the convex hull formed by D and S_B(D). Therefore, the feed compositions that exhibit multiplicities lie in the union of all the convex hulls formed by D and the corresponding S_B(D). In Figure 4 the appropriate feed region is shaded.

3 Finite Reflux and Finite Number of Trays

In this section, first we present steady state bifurcation results for the mixture acetone (L) - heptane (H) - benzene (I-E) which show that the prediction for the existence of multiple steady states in the ∞/∞ case carries over to columns operating at finite reflux and with a finite number of trays. We further show that, although the predictions were made in the ∞/∞ case, it does not mean that multiple steady states do not

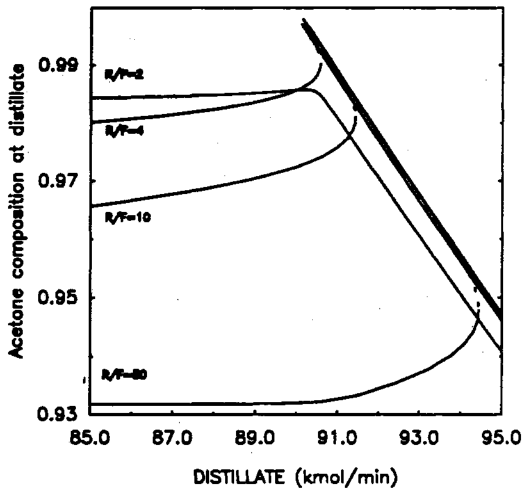

Figure 5: Bifurcation diagrams for a column with N=44 trays, E/F =1 and various R/F. The distillate flow is the bifurcation parameter.

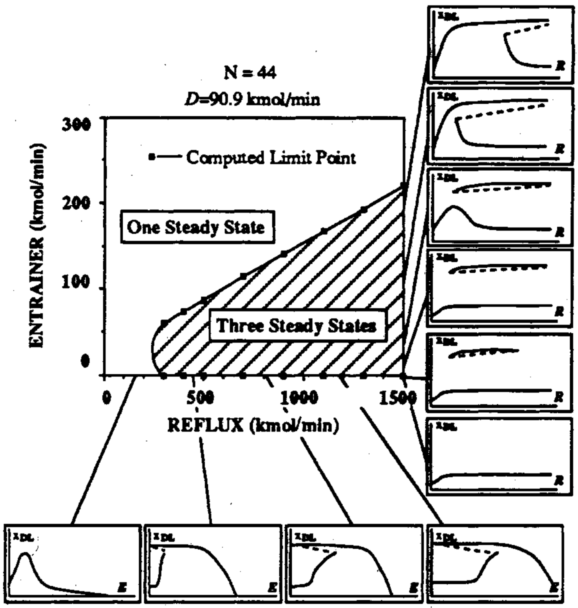

Figure 6: Entrainer - Reflux Multiplicity Region and typical bifurcation diagrams with the entrainer and reflux flows as the bifurcation parameters.

exist for realistic operating conditions (low reflux and number of trays). However, apart from the fact that the ∞/∞ case predictions carry over, the results presented here should not be generalized because they are specific to the particular example. The bifurcation calculations were conducted with AUTO, a software package developed by Doedel (1986).

Varying the Distillate Flow

Figure 5 shows typical bifurcation diagrams with the distillate flow as the bifurcation parameter. If R is low enough (R/F =2), a unique steady state is calculated by the continuation algorithm. For higher values of R (R/F =4, 10, 50), multiple steady states exist for some D. In these cases, a unique stable steady state exists for low D. D increases until the continuation algorithm reaches the first limit point. Beyond that point an unstable steady state is calculated (dashed curve). Beyond the second limit point, D increases again and a second stable steady state is calculated. Hence, two stable and one unstable steady states exist for distillate flows between the two limit points (multiplicity region); a unique stable steady state exists otherwise. Note that, although those multiple steady states were predicted at infinite reflux, they still exist at very low reflux values.

Varying the Entrainer and Reflux Flows

The bifurcation calculation results are summarized in Figure 6. The four pictures at the bottom of Figure 6 show typical bifurcation diagrams with the entrainer feed flow as the bifurcation parameter for various fixed reflux flows. At very low reflux, a unique stable steady state exists for all entrainer feed flows. As the reflux increases, three steady states appear for some entrainer feed flow interval. The six pictures on the right side of Figure 6 show typical bifurcation diagrams with the reflux flow as the bifurcation parameter for various entrainer flows. In the upper four pictures, three steady states exist for reflux flows above the limit point (and persist at infinite reflux) while a unique stable steady state exists for reflux flows below that limit point. At very low entrainer flows, the three steady states do not extend to infinite reflux and at even lower entrainer flows, a unique steady state exists throughout (two lower pictures). Finally, the central picture of Figure 6 shows the entrainer-reflux multiplicity region. Note that multiplicities persist for low entrainer and reflux flows which is the region of operation in practice.

Effect of the number of trays

In the first part of this article we have shown that multiplicities exist for columns with an infinite number of trays. Doherty and Perkins (1982) proved that multiplicities cannot exist for single-staged "columns." It is expected then, that multiplicities vanish as the number of trays decreases below some critical number. The effect of decreasing the number of stages is depicted via bifurcation diagrams where the distillate and reflux flows are fixed and the entrainer flow is the bifurcation parameter. Figure 7 shows four such diagrams for columns with different number of stages. Three steady states exist for some very narrow entrainer flow interval for the columns with 23 and 22 trays while multiplicities vanish for the 21 and 15 tray columns.

Curved Boundaries

In this subsection we present an example which illustrates that highly curved boundaries can induce multiplicities. The ternary mixture under consideration is that of acetone (L), methanol (H) and chloroform (I) also studied by Kienle et al. (1992). The interior residue curve boundaries divide the composition triangle in four distillation regions. Figure 8 shows the

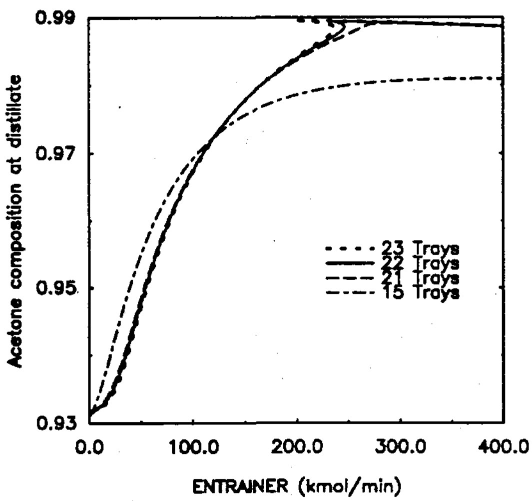

Figure 7: Vanishing multiplicity in small columns with R =1500 kmol/min and D =90.9 kmol/min.

region confined by the chloroform - methanol azeotrope (unstable node), the ternary saddle azeotrope, the acetone - chloroform azeotrope (stable node) and the pure chloroform corner (saddle). The highly curved boundary between the ternary and the acetone - chloroform azeotropes induces the existence of multiple steady states. This is supported by simulation results for a column with 30 trays, D/F =.5, R/F =100, a feed composition of 26.5% acetone, 23% methanol and 50.5% chloroform and a feed tray located at stage 14. Figure 8 shows the location of the three different column profiles (two stable and one unstable) relative to the distillation region boundaries in the composition triangle.

4 Conclusions

In this article we study multiple steady states in ternary homogeneous azeotropic distillation. First we examine in detail the infinite reflux and infinite number of trays (∞/∞) case. More specifically, we answered the following questions: Given a ternary mixture and its residue curve diagram,

(1) find whether multiple steady states exist for some feed composition and

(2) locate the feed composition region that lead to these multiple steady states.

We derive (1) the necessary and sufficient geometrical condition for the existence of multiple steady states and (2) the condition the feed compositions must satisfy to lead to multiple steady states.

We use an example to show that the prediction for the existence of multiple steady states in the ∞/∞ case carries over to columns operating at finite reflux and with a finite number of trays. We further show that, although the predictions were made in the ∞/∞ case, it does not mean that multiple steady states do not exist for realistic operating conditions (low reflux and entrainer feed flows and small number of trays).

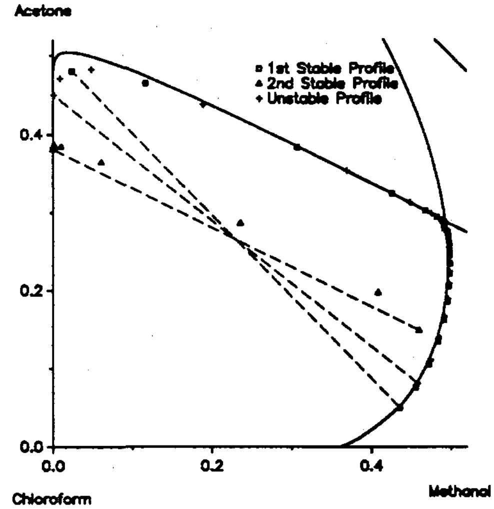

Figure 8: The three steady states of the Acetone / Methanol / Chloroform column with N=30 trays, E/F =.5 and R/F =100. in the composition triangle.

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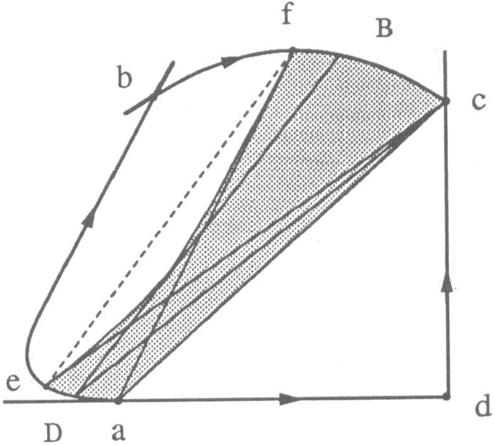

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